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The Extraction of Potash  
from Feldspar by Agitation with  
Lime under Steam Pressure

Chemistry

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THE EXTRACTION OF POTASH FROM FELDSPAR BY AGITATION  
WITH LIME UNDER STEAM PRESSURE

BY

GEORGE HENRY MENGEL

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

IN

THE COLLEGE OF LIBERAL ARTS AND SCIENCES

OF THE

UNIVERSITY OF ILLINOIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

GEORGE HENRY MENGEI

ENTITLED The Extraction of Potash From Feldspar by Agitation

With Lime Under Steam Pressure.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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1915

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THE EXTRACTION OF POTASH FROM FELDSPAR BY AGITATION  
WITH LIME UNDER STEAM PRESSURE

Introduction

Dr. T. R. Ernest<sup>1</sup> in his work on silica brick found that under high steam pressure, lime reacted with silica to form silicates. It was thought that this reaction might apply equally well to minerals high in silica and also containing other valuable constituents, for example potassium in the feldspars. This was one phase of Mr. A. W. Beemer's<sup>2</sup> work. He showed, by qualitative tests, that calcium hydroxide did react with feldspar when placed under steam pressure, producing soluble potassium compounds. Mr. F. L. Roman<sup>3</sup> investigated this reaction and tried to find the best conditions under which the reaction took place and determine the amount of potassium rendered water soluble. Mr. Roman made briquettes of his materials and placed these under steam pressure. He studied the effects of varying proportions and varying steam pressures. Mr. R. J. Quinn<sup>4</sup> investigated the claims of a number of patents on this subject testing them under as uniform conditions as possible.

The object of this thesis is to continue the work indicated above. As a result of the work of Mr. Roman and Mr. Quinn, it was thought that an increase of water soluble potash could be obtained by agitating a slurry mixture of the reacting materials. The work of this thesis will be as follows:

1. A summary of the sources of potash.
2. A review of the current literature dealing with this problem.

1- Thesis University of Illinois, 1908.

2- Thesis University of Illinois, 1910.

3- Thesis University of Illinois, 1911.

4- Thesis University of Illinois, 1912.



3. An experimental investigation on the possibility of extracting the potash from feldspar by means of agitating with calcium hydroxide under steam pressure, studying the effect of the following factors on the completeness of reaction of

- a. time
- b. variation of pressure
- c. changing ratio of lime to feldspar
- d. additions of soluble electrolytes

and studying the possibility of utilizing the insoluble residue after extraction.

#### Sources of Potassium Compounds

In reviewing the literature on the potash question, one is impressed by the fact that at present the world's supply comes from the Stassfurt deposits in Germany. These deposits constitute the only known extensive source of potassium compounds. The entire deposits are controlled by a syndicate under governmental control, and American users have repeatedly had friction with the syndicate. Likewise the European War has cut off the supply for an indefinite time. The desirability of having a supply independent of Germany can readily be appreciated when we consider that in 1911 we imported a total of 1,025,154 tons of potassium salts. This condition has stimulated investigation for an independent supply for the United States.

According to F. W. Clark<sup>1</sup> the average percentage of potash ( $K_2O$ ) in the earth's crust is three percent. This is the average value of 1434 analyses. The more common minerals bearing potash are

1- U.S. Geological Survey - Bull. 530. B. 1911.



listed by Cushman and Hubbard<sup>1</sup> as follows:

Orthosilicates.

Kaliophilite	27	- 29%	K <sub>2</sub> O
Microsommitite	6	-	7.8
Haiynite	0	-	4.96
Algenite	0	-	9.97

Metasilicates

Leucite	18.9	-	21.5
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Polysilicates

Orthoclase	5.4	-	15.9
Microcline	5.4	-	15.9
Hyalophan	7.8	-	11.7
Anorthoclase	2.5	-	11.9

Hydrous Silicates

Muscovite	6.8	-	11.1
Lepidolite	10.6	-	12.3
Zinnwaldite	10.4	-	10.6
Biotite	6.2	-	10.1
Phlogotite	7.0	-	10.3
Zeolites	0.0	-	11

Of these minerals orthoclase constitutes 15% of the earth's crust, and has the formula K<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.6SiO<sub>2</sub>. Usually some of the K<sub>2</sub>O is replaced by other bases as the oxides of sodium calcium, or magnesium. There are immense deposits of this mineral in different parts of our country and H. S. Gale<sup>2</sup> discusses these deposits in detail.

1- "Extraction of Potash from Feldspathic Rocks". J.Amer. Chem. Soc. Vol. 30 - P. 779-1908.

2- U.S. Geological Survey Bull. 540 N.



The deposits of lencite are also large and extensive. The mineral is a potassium aluminium silicate with a formula of  $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ .

The green sand Marls of New Jersey consist mostly of glauconite which contains about 3%  $K_2O$  in a somewhat soluble form, but high freight rates makes its use prohibitive except locally.

J. W. Turrentine<sup>1</sup> has listed most of the saline waters of the United States with reference to their potassium content. None of the salines or bitterns give any promise of a supply of potassium. At Searles Lake<sup>2</sup> which is in California, was found a brine which contained considerable potassium chloride along with other minerals. The California Trona Company was organized to work this lake bed deposit. They have erected an experimental plant and expect to put their products on the market soon.

W. C. Phalen<sup>3</sup> in reviewing the potash situation discusses the deposits of alunite,  $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ , recently found at Marysvale, Utah. Alunite is a slightly soluble potassium aluminium sulphate, which on being roasted is converted into a more soluble form. This deposit will be worked in the near future by a number of companies organized for its development. Some alunite has also been found not far from Marysvale in the locality known as Sheeps Rocks, but the extent of the deposit is unknown.

The kelps of the Pacific coast have also been suggested as a source of potassium compounds. Two varieties, the *nereocystis luetkana* and *macrocystis pyrifera* have been found to contain notable

1- U.S. Dept. of Agr. Bur. of Soils. Bull. 94.

2- Searles Lake Potash Deposit. C. E. Dolbear. Eng. and Min. Jour. Vol. 95 - P. 259-1913.

3- Chem. Eng. Vol. 20 - P. 89. 1914.

4

quantities of potassium along with some iodine. The contents based on dry weight of kelp are:

	KCl	I
<i>Nereocystis Luetkana</i>	30%	.16%
<i>Macrocystis pyrifera</i>	15%	.32%

The kelp fields are very extensive and could undoubtedly supply the Pacific coast with potash salts. When the kelp is left to dry on the shore the potassium chloride crystallizes out on the leaves and stems and can be shaken off. A small plant has been erected in which the dried kelp is burned and from the residue the potassium chloride is leached out. A complete report on this source of potash has recently been issued by Cameron.<sup>1</sup>

Some lesser sources of potash are wool washings, beet sugar wastes, wood ashes and cement flue dust. Recovery of by-products in the wool washing water has been forced on to a number of manufacturers on account of stream pollution. The amount of potassium recovered is small. Wood ashes at one time supplied all our needs for potash salts but this source is no longer important. Beet sugar wastes have never been thoroughly investigated and no data is available. The flue dust from cement mills has been found to contain appreciable amounts of volatilized potassium salts and this fact has been the cause of considerable speculation as to whether potash could be made a by-product of the cement mills or vice versa.

The feldspathic rocks represent the most promising field for work and the only large potential supply of potassium. A number of general methods of attack have been proposed and numerous patents

1- Potash From Kelp Frank K. Cameron, U.S. Dept. of Agr., Bureau of Soils, Report No. 100. Apr. 10, 1915.



have been issued having as their object the production of soluble potassium salts from this source. These general methods may be classified as follows:

1. Fine grinding -- Wet and dry
2. Electrolytic treatment
3. Acid treatment
4. Fusion with a flux
5. Changing the internal structure by heating and chilling.
6. Sintering
7. Use of pressure with suitable reagents.

A brief but incomplete review of some of the work along these indicated lines will be given.

#### Fine Grinding

Mr. Roman in his thesis investigated the effect of fine grinding on the percentage of extraction and found varying results. He used a mixture of one part calcium hydroxide and one part feldspar. This mixture was placed in a ball mill and ground for three hours. One experiment gave a higher extraction and another gave a lower extraction than was obtained without fine grinding. Cushman and Hubbard<sup>1</sup> have shown in their work on road materials that rock powders when moistened, form with silica hydrated compounds of a colloidal nature which retain potassium compounds even when they are in a soluble form, so that only a very small amount of potassium is capable of extraction.

Cushman and Hubbard<sup>2</sup> give results of a series of experiments

1- U.S. Dept. of Agr. Office of Public Roads. Bull. 28.

2- "Extraction of Potash from Feldspathic Rocks." Jour. Amer. Chem. Soc. Vol. 30 - P. 779.



which they conducted with feldspar powders in varying degrees of fineness and with a number of electrolytes. These powders were slimed and placed in an electrolytic cell. This cell was made up of a thin walled wooden cylinder within a larger one. The inner cylinder which contained the slurry was made the anode and the outer the cathode. The potassium and sodium passed out of the anode chamber into the cathode chamber. After running the cell awhile the reaction slowed up presumably due to the presence of colloid matter and it became necessary to use accelerators. They agitated the mixture but this was not as effective as the addition of small amounts of hydrofluoric acid, of which only one tenth of the amount necessary for the silica present, was required. The authors concluded that electrolytic extraction was not feasible commercially on account of high current consumption. They recommend further study with hydrofluoric acid.

#### Acid Treatment

The feldspars are only sparingly soluble in acids, but a number of patents using acids as the solvent have been taken out. John Spiller<sup>1</sup> proposed to manufacture potash alum by heating a mixture of feldspar and sulphuric acid along with some fluorspar. Silicon tetrafluoride was to be a by-product.

W. T. Gibbs<sup>2</sup> proposed a method in which he decomposed his feldspar by means of a catalytic agent. For his solvent he used a liquid containing from two to four percent hydrofluoric acid and fifty percent sulphuric acid, the balance being water. Mr. Quinn worked on this plan and obtained fifty seven percent extraction with

1- "Feldspar as a Source of Potash" Jour. Soc. Chem. Ind. Vol. 1,

P. 129

2- U. S. Patent 772612. Ger. Patent 173902.



feldspar and seventy percent extraction with leucite rock.

H. W. Foote and S. R. Scholes<sup>1</sup> give some results in which they claim as high as one hundred percent extraction. These authors worked with hydrofluoric acid in sealed glass tubes.

The use of acid gases has been proposed by at least two investigators. H. E. Ashley<sup>2</sup> suggests the use of the large quantities of sulphur dioxide from smelter stacks. H. S. Blackmore<sup>3</sup> plans to use carbon dioxide under five hundred pounds pressure which is to be applied intermittently.

#### Heating to Change Structure

R. F. Carpenter<sup>4</sup> claimed that by altering the internal structure by heating to redness and chilling rapidly the potash could be leached out.

A. J. Swayze<sup>5</sup> uses a process in which he heats feldspar as in the Carpenter method and subsequently heats his product with potassium hydroxide. He obtains potassium silicate and aluminate. Mr. Quinn tried out this method as follows: The feldspar was heated up to 900°C for an hour and heated with potassium hydroxide for three and one half hours under pressures varying from seventeen to twenty five atmospheres with the result that only thirty five percent was extracted.

#### Fusion with Volatization of Potash Salts

In 1905 A. J. Swayze<sup>6</sup> obtained a patent in which he treated

1- "Extraction of Potash and Alumina from Feldspar" Jour. Ind. and Eng. Chem. Vol. 4, P.372.

2- Decomposition of Clay and Utilization of Amelter Smoke." Jour. Md. and Eng. Chem., Vol. 3, P.91.

3- U.S. Patent 862676.

4- U.S. Patent 959841.

5- U.S. Patent 862676.

6- U.S. Patent 789074.



feldspar with gypsum and carbon and fused the mass. The potassium sulphate formed was to be volatilized and collected.

Spencer and Eckel<sup>1</sup> mixed sand and potash-bearing marls in proper proportions for a cement mix, and volatilized the potash salts. In 1911 Eckel<sup>2</sup> varied this slightly by adding green sand marls to a cement mix and volatilizing the potassium salts. Eckel<sup>3</sup> took out a second patent in 1911 in which he produces potassium sulphate from green sand marls, calcite and carbon by fusing the mass and volatilizing the potassium salts.

Recently S. Peacock<sup>4</sup> obtained a patent in which he attempts to solve both the potash and the nitrogen fixation problems. He uses a mixture of feldspar and carbon in an atmosphere of nitrogen in a furnace similar to the Serpek furnace for producing aluminum nitride. For each pound of alumina in the feldspar Peacock uses <sup>of a pound</sup> seventy five hundredths/carbon, for each pound of potash three tenths pound carbon, and for each pound of silica eight tenths pound carbon. This mass is heated in an atmosphere of nitrogen to 2500°C forming first, potassium carbide which is converted to the carbonitride having a formula of  $K_6N_2C_3N_4$ . The carbonitride is volatilized and collected and then treated with superheated steam under seven to nine atmospheres pressure, potassium carbonate and ammonia being formed. The inventor also proposes to form silica compounds from the residue by raising the temperature of the furnace.

#### Sintering

In this class are placed those operations in which the mix

1-U.S. Patent 912266.

2-U.S. Patent 1011172.

3-U.S. Patent 1011173.

4-U.S. Patent 1129506.



is heated to incipient fusion and apparently little changed in outward physical appearance. Some very promising work has been accomplished in this phase of the problem.

In a paper by J. G. Rhodin<sup>1</sup> some results of his work are given. He treated feldspar with calcium oxide and sodium chloride and heated the mixture to a point below fusion. He obtained very good results with a mixture of one part feldspar, four tenths part lime and an equal amount of salt, which he heated for one hour at 900°C. He claims seventy five percent extraction and also claims the residue on the further addition of silica to be suitable for glass making.

Wadman<sup>2</sup> treated lepidolite with potassium sulphate and sulphuric acid. He claimed to have rendered the potassium, water soluble. McKee<sup>3</sup> treated mica with lime, salt, and carbon. The product was potassium chloride. Thompson<sup>4</sup> treated feldspar with acid sodium sulphate and salt at red heat. He claimed to have produced potassium sulphate. Hart<sup>5</sup> treated feldspar with barites, carbon and sulphuric acid to form potassium sulphate.

Cushman and Coggeshall<sup>6</sup> have worked out a method in which a mixture of one hundred parts feldspar, twenty parts lime and ten to twenty parts rock salt, are treated with a strong solution of calcium chloride in a special "clumping" device. The clumps are held together by means of an oxychloride cement. They are separated by screening and are sintered by passage through a cement kiln. The

1- J. Soc. Chem. Ind. Vol. 20 - p. 440. U.S. Patent 641406.

2- U. S. Patent 847856.

3- U. S. Patent 869011.

4- U. S. Patent 995105.

5- U. S. Patent 997761.

6- "Production of Available Potash from Natural Silicates", Jour. Ind. and Eng. Chem. Vol. 4, p. 821.



authors claim over seventy five percent extraction. This method has been tried on a large scale and the costs of operation are apparently less than the corresponding costs for cement manufacture.

#### Pressure Methods.

In 1904 Levi<sup>1</sup> patented a method whereby he treated feldspar with calcium hydroxide and sodium hydroxide under sixteen atmospheres pressure obtaining potassium silicate. Gibbs<sup>2</sup> treated feldspar with calcium hydroxide and steam, obtaining potassium hydroxide.

Dr. F. Friedensburg<sup>3</sup> discusses some of the proposed methods and classifies them under the heads of possible, improbable and ridiculous. This characterization seems to agree well with the facts.

#### Experimental Work

In the experimental work it was planned to investigate the effect of varying a number of working conditions as has already been suggested. As steam pressure up to one hundred pounds was available, extractions were to be made under different pressures; also for different lengths of time under the same pressure. The effect of electrolytes of lower atomic weight than the potassium was likewise to be investigated, similarly the ratio of lime to feldspar. If possible tests were to be made on the residue with a view to its ultimate utilization.

#### Analytical Methods

In a work of this kind where a large number of potassium determinations are made, a method of analysis must be used in which

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1- French Patent 344246.

2- U. S. Patent 910662.

3- "Kaligeinnung ares Silicaten" Chem. Ind. Vol. 36 - p. 467.



the reagents are cheap, the manipulation simple, and the results accurate. This precluded the chlorplatinate method for determining potassium on account of the labor involved in freeing the solution of interfering elements and also because the reagents are expensive. The cobalti-nitrite method was used by Mr. Roman and Mr. Quinn with somewhat unsatisfactory results. Moreover, the literature is full of controversy with regard to the exact nature of the compound formed, therefore, it was deemed best to use a different method. The method finally selected was the perchlorate methods as modified by Scholl.<sup>1</sup> This method was found to be accurate and rapid and gave good checking results.

#### Materials

The materials used in this investigation consisted of Brandywine Summit feldspar ground for potters use and a very pure grade of lime. The same feldspar was used by Mr. Roman and Mr. Quinn. The analyses are as follows:

	1911	1912	1915
	Roman	Quinn	Mengel
SiO <sub>2</sub>	70.02	69.56	70.04
Al <sub>2</sub> O <sub>3</sub>	17.89	17.84	16.09
CaO	.98	1.14	.54
MgO	.16	.41	.12
Fe <sub>2</sub> O <sub>3</sub>	.21	.25	.38
Na <sub>2</sub> O	1.61	1.67	2.19
K <sub>2</sub> O	8.71	8.90	9.81
Loss on Ignition	<u>.38</u>	<u>.50</u>	<u>.72</u>
	99.96	100.27	99.89

1- Jour. Amer. Chem. Soc. Vol. 36 - p. 2085. 1914.



### Apparatus

It was planned to use in this work a small autoclave with a stirrer, which had been ordered in Germany, but owing to the disturbances due to the European War it was not received until April. Attempts to utilize a small autoclave without a stirrer belonging to the department only resulted in a loss of time. An experiment was tried of fitting the apparatus with an electromagnetic stirrer. A heavy coil of number eight insulated copper wire was placed around the body of the autoclave and an iron bar placed within the vessel. When the current was turned on, the bar was drawn to the side on account of an iron flange acting as a condenser for the lines of magnetic force and it was not possible to secure up and down motion needed for proper stirring. It had been expected that by a suitable make and break arrangement the bar would be alternately raised and dropped and thereby secure a stirring action. Next it was planned to fit the autoclave with a mechanical stirrer but on account of difficulties inherent in the design of the apparatus the matter was dropped. Then it was determined to adopt for use the autoclave used by Dr. Ernest. This autoclave was taken to Burr and Co., and altered as shown in the blue print, plate number one. The details are lettered. The steel shaft C is rotated by an iron pulley C and is held in place by a lock-nut at the top and by a seat at the bottom. The paddles labeled A, are of cast iron and are adjustable being fastened onto the shaft by means of set screws. The discharge pipe is marked D and the steam inlet pipe and gauge marked E. and G respectively. The insulation is marked H.

### Experimental Procedure

The method used was as follows: a slurry mixture consisting



of five hundred grams of lime and one thousand grams feldspar was placed in the autoclave which was then closed tightly. Ninety pounds steam pressure was turned on and the mixture agitated for the predetermined time. In spite of good insulation, when the autoclave was run for a period of more than an hour there was considerable condensation of steam in the vessel. This greatly altered the concentration of the substance during the experiment. The slurry was drawn off and filtered through a small filter press. The resulting solution, usually five gallons or more was placed in a suitable container and evaporated to dryness.

The material which had been thus evaporated was taken up in water and filtered to remove calcium carbonate. The filtrate was then made up to one liter and an aliquot part taken for analysis. The analysis was made as follows: Twenty five cubic centimeters were pipetted off and to this was added ammonium hydroxide, carbonate and oxalate. The precipitate was filtered off and the filtrate evaporated to dryness and ammonium salts expelled by heating. The residue was taken up in hydrochloric acid and again filtered. To the filtrate was added perchloric acid and it was evaporated to white fumes. The potassium perchlorate was washed into a weighed Gooch crucible with absolute alcohol containing two tenths of one percent of perchloric acid. The crucible and contents were heated for one hour at 135°C.

#### Difficulties

The difficulties and obstacles were more in evidence than work accomplished. Some of these have already been mentioned in regard to obtaining suitable apparatus. When the autoclave was set up the department had no motor available of sufficient power to turn



the stirring mechanism; and one was borrowed from the electrical engineering department. A month passed before the motor could be set up for use. Asbestos was recommended as a packing material, but unlubricated asbestos threads seemed to take hold of the shaft and be pulled out of place so that it did not hold the pressure. Then asbestos threads were soaked with raw linseed oil containing some graphite in suspension. This gave better, but still unsatisfactory, results. The packing finally used was a commercial packing known as "Palmetto" which gave excellent results. After a trial run it was found necessary to insulate the cylinder on account of the large amount of condensation of steam. This was done by shredding asbestos coverings as used on steam pipes and allowing the material to become sticky by adding a small quantity of water to it. Before applying to the cylinder of the autoclave some cement was added. A coating of this material about one inch in thickness was placed on the cylinder and this was found to give fairly satisfactory heat insulation. Whenever the apparatus had been used, it was impossible to remove the stirrer without having the paddles drop off. This was due to the fact that shaft and paddles were made of different materials and had different coefficients of expansion. After the paddles had dropped into the cylinder it was difficult to remove them because the depth of the vessel made it necessary to use tongs to reach them. Only once did the paddles stay on the shaft and that time they were held by wooden wedges forced between them and the shaft.

#### Results

The work actually accomplished was to find the effect of time of treatment on a mixture of five hundred grams of lime and one



thousand grams of feldspar treated under an average of ninety pounds steam pressure for periods varying from one to ten hours.

The results are as follows:

Time of treatment	% Extraction
1 hr.	5.60
2	19.15
3	9.10
4	1.95
10	1.24

These results are somewhat contrary to what Roman found. In his conclusions Roman states that, "The action of the lime on feldspar increases to a certain extent with the steam pressure and the length of treating." The values here obtained show that a secondary reaction takes place. It is possible that the soluble salts which are formed, are absorbed by colloids of either the silicic acid or aluminum hydroxide which are present. As a lack of time prevented the completion of the work planned no results were obtained from which further conclusions could be drawn.



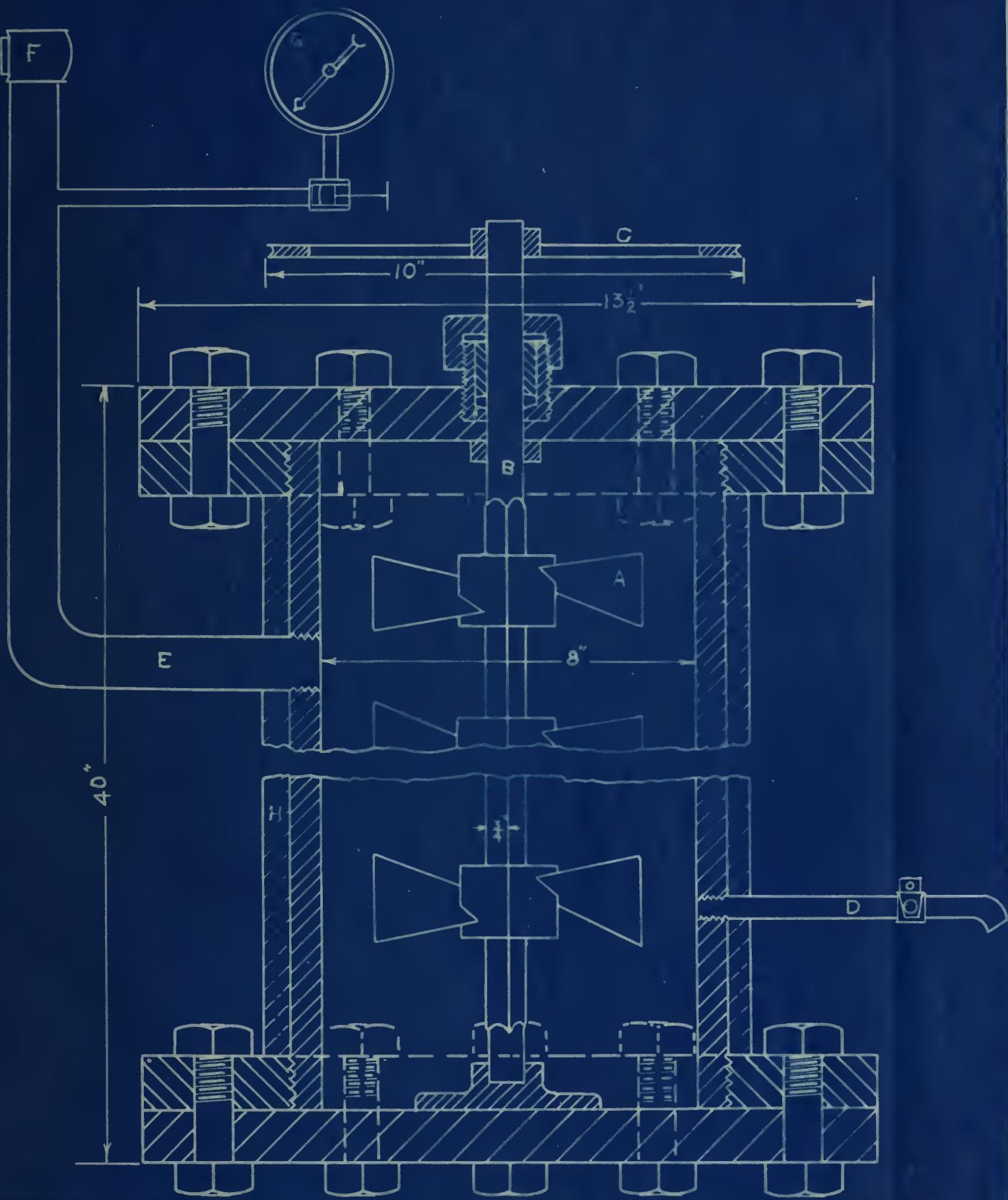


TABLE I





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